

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**



PATENT ABSTRACTS OF JAPAN

(11) Publication number: 11118761 A

(43) Date of publication of application: 30 . 04 . 99

(51) Int. Cl.

G01N 27/447

(21) Application number: 09281526

(22) Date of filing: 15 . 10 . 97

(71) Applicant: YOKOGAWA ANALYTICAL SYSTEMS INC

(72) Inventor: SOGA TOMOYOSHI

(54) METHOD AND DEVICE FOR ANALYZING IONS
DUE TO CAPILLARY CATAPHORESIS

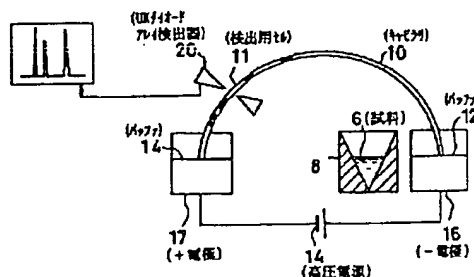
condition.

COPYRIGHT: (C)1999,JPO

(57) Abstract:

PROBLEM TO BE SOLVED: To simultaneously analyze an anion and a metal ion using cataphoresis by using an anion substance with a high complex stability constant to metal ions for a cataphoresis buffer liquid as the complex between the metal ions and anion property.

SOLUTION: A sample 6 is loaded into a sample container 8 and is sealed, and the inside of the container 8 is pressurized and a buffer 12 at a cathode side is injected. Since the complex formation reaction of PDC (2,6-pyridine carboxylic acid) in the buffer 12 is fast, a complex can be formed immediately when the sample 6 is injected into a capillary 10 and is mixed with the PDC. A UV diode array detector 20 consists of a lens 24 for setting the light of a light source 22 into parallel beams, an optical slit 28 for alignment interface for aligning measurement rays by a shutter 26 and a cell 11 for detection of the capillary 10, a diffraction grating 30 for diffracting measurement rays according to the wavelength, and a diode array 32 for detecting the diffracted light at each wavelength, thus performing analysis with a single device and a single analysis



NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

LAIMS

Claim(s)]

Claim 1] Ion analytical method by the capillary electrophoresis characterized by analyzing anions and metal ions simultaneously by facing analyzing ion using capillary electrophoresis, using for the migration buffer solution the anion nature matter which has a high complex stability constant to metal ions, and making the complex of metal ions and anion nature form.

Claim 2] Ion analytical method by the capillary electrophoresis to which said anion nature matter is characterized by being 2, 6-pyridinecarboxylic acid, ethylenediaminetetraacetic acid, or nitrilotriacetic acid in claim 1.

Claim 3] The ion analysis apparatus by the capillary electrophoresis characterized by to have the migration buffer solution with which the anion nature matter which has a high complex stability constant to metal ions was used in the equipment which analyzes ion using capillary electrophoresis, the capillary which separates the ion poured into this migration buffer solution, and the detector which analyzes the separated anions and metal ions simultaneously by this capillary appearance side.

Claim 4] The ion analysis apparatus by the capillary electrophoresis characterized by being the diode array detector in which measurement according [said detector] to both indirect extinction method and direct detection method is possible in claim 3.

[translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

DETAILED DESCRIPTION

Detailed Description of the Invention]

[001]

[Field of the Invention] This invention relates to the approach and equipment which analyze ion using capillary electrophoresis, and relates to the ion analytical method and equipment by capillary electrophoresis which can measure simultaneously anions, such as an organic acid, a fatty acid, aromatic carboxylic acid, and an inorganic anion, and metal ions, such as nickel, cobalt, copper, and zinc, especially.

[002]

[Description of the Prior Art] Conventionally, anion nature matter, such as an organic acid and an inorganic anion, was measured using separation analysis equipments, such as ion chromatography and capillary electrophoresis, and, on the other hand, the cation nature matter containing metal ions, such as nickel, cobalt, and copper, was measured using separation analysis equipments, such as elemental-analysis equipments, such as atomic-absorption-analysis equipment, inductively-coupled-plasma-atomic-emission-spectrometry equipment (ICP/AES), and inductively-coupled-plasma-source-mass-spectrometry equipment (ICP/MS), or ion chromatography, and capillary electrophoresis.

[003]

[Problem(s) to be Solved by the Invention] However, since the anions and metal ions from which ionicity differs were not able to be measured simultaneously, a measuring device and conditions were required for at least two, and the number of equipment needed to increase, or it needed to measure by having changed the Measuring condition, and had troubles, like measurement takes time amount.

[004] This invention was made so that it may cancel said conventional trouble, and it makes it a technical problem to enable it to analyze anions and metal ions simultaneously using capillary electrophoresis.

[005]

[Means for Solving the Problem] This invention solves said technical problem by facing analyzing ion using capillary electrophoresis, using for the migration buffer solution the anion nature matter which has a high complex stability constant to metal ions, and making the complex of metal ions and anion nature form.

[006] Moreover, let said anion nature matter be 2, 6-pyridinecarboxylic acid, ethylenediaminetetraacetic acid, or nitrilotriacetic acid.

[007] Moreover, similarly in the equipment which analyzes ion using capillary electrophoresis, said technical problem is solved by having the migration buffer solution with which the anion nature matter which has a high complex stability constant to metal ions was used, the capillary which separates the ion poured into this migration buffer solution, and the detector which analyzes the separated anions and metal ions simultaneously by this capillary appearance side.

[008] Moreover, it can be made to perform measurement of high degree of accuracy with a single detector by using said detector as the diode array detector in which measurement by both indirect extinction method and direct detection method is possible.

[009] 2, 6-pyridinecarboxylic acid (PDC), ethylenediaminetetraacetic acid, It is a high complex stability constant (it is used best as what shows the stability in the solution of a complex) to metal ions, such as nitrilotriacetic acid. it expresses with the inverse number of the dissociation constant of a complex -- having -- it has, and by using the high anion nature matter of metal ions and complexing ability for the migration buffer solution (buffer), the nickel in a sample, cobalt, a copper ion, etc. form PDC and a complex, and as shown in drawing 1, they show anion nature. Therefore, it becomes possible to measure to an organic acid and coincidence, such as inorganic anions, such as chloride ion and sulfate ion, and

malic acid, a citric acid, an acetic acid.

010] The complex stability constant to each metal of PDC which can be used for a buffer is shown in drawing 2.

011] For example, PDC metal complexes, such as PDC and nickel, have ultraviolet (UV) absorption, and in the wavelength of 275nm, and 225nm, since UV absorption is larger than PDC of a buffer, as shown in drawing 3 (A), a peak appears above the base line. On the other hand, in anions, since UV absorption is smaller than PDC, a peak appears below the base line. However, by choosing measurement wavelength, the upper and lower sides can be reversed, and as shown in drawing 3 (B), anions can also be expressed to an upside.

012] Drawing 3 (A) is the case where drawing 3 (B) is based on the indirect extinction method of the measurement wavelength of 350.20nm, and 275.10nm of reference wave length, when based on the measurement wavelength of 275.10nm, and the direct detection method of reference wave length OFF.

013]

[Embodiment of the Invention] With reference to a drawing, the operation gestalt of this invention is explained to a detail below.

014] The whole ion analysis apparatus configuration by the capillary electrophoresis built over this invention at drawing 4 is shown.

015] This operation gestalt with the capillary 10 for separating a sample, and the sample 6 in a specimen container 8. The buffers 12 (cathode side) and 13 (anode plate side) for being introduced into this capillary 10 and separating a sample. To the platinum electrodes 16 (cathode side) and 17 (anode plate side) of said capillary 10 ends, for example, the high voltage power supply 14 which impresses the high tension of 5-30kV. It is constituted including the cell 11 for detection which removed the outer wall (for example, polyimide) of said capillary 10, and was formed, and UV diode array detector 20 in which measurement by both indirect extinction method and direct detection method is possible.

016] The sample 6 inserted in said specimen container 8 is poured into the buffer 12 by the side of cathode by sealing and covering with a lid 9 to this specimen container 8, and pressurizing the inside of a specimen container, as shown in drawing 5. Since the complexing reaction of PDC in a buffer is quick, if a sample 6 is poured in into a capillary 10 and mixed with PDC, a complex will be formed immediately.

017] The light source 22 which consists of deuterium lamps as said UV diode array detector 20 is shown in a detail at drawing 6. The lens 24 for making into a parallel ray light generated from this light source 22, the shutter 26 for turning a measuring beam line on and off, and the cell 11 for detection of said capillary 10 by the way. The optical slit 28 for an alignment interface for ready-aligning a measuring beam line. It is constituted using the diode array 32 whose measurement wavelength is 190-600nm in order to detect the light diffracted by the diffraction grating 30 and this diffraction grating 30 for diffracting the measuring beam line which passed this optical slit 28 according to wavelength for every wavelength.

018]

[Example] As buffers 12 and 13, 20mMPDC and the 0.5mM cetyl trimethylammonium salt's picture pH 5.77 were used, using the fuze DOSHIRIKA capillary of the bore of 50 micrometers, the outer diameter of 350 micrometers, the overall length of 80.5cm, and 72cm of effective length to the cell 11 for detection as said capillary 10. Applied voltage measured the temperature of 25kV and a capillary 10 at 20 degrees C. The sample was poured in for 8 seconds by 50mbar using the inflatable flexible bag technique as shown in drawing 5. The indirect extinction method of the measurement wavelength of 350.20nm and 275.10nm of reference wave length was used for detection of the matter which has almost no UV absorption like sulfate ion or organic acids in detection of the matter which has UV absorption like nickel ion in detection using UV diode array detector 20 using the measurement wavelength of 275.10nm, and the direct detection method of reference wave long OFF. Drawing 3 shows the example of measurement of the organic-acid standard solution in this example.

019] Moreover, the example of simultaneous analysis of the anions in the non-electrolyzed nickel-plating liquid diluted 100 times and nickel ion is shown in drawing 7.

020] The approach of this operation gestalt and the comparison result of the quantum value of the nickel in the non-electrolyzed nickel-plating liquid measured by conventional ICP/MS are shown in drawing 8. Both analysis result is well in agreement so that clearly from drawing.

021] Moreover, the example of simultaneous analysis of the anions in the non-electrolytic copper plating liquid of 500 times dilution and a copper ion is shown in drawing 9.

022] In this operation gestalt, since UV diode array detector is used as a detector, measurement by both indirect

inction method and direct detection method is possible at one detector, and a configuration is simple.

023] In addition, the class of detector is not limited to this. Measurement wavelength is also limited to neither an operation gestalt nor an example. The class of capillary is not limited to a fused DSHIRIKA capillary, either. It is possible to use other anion nature matter in which a buffer is not limited to PDC, either but has a high complex stability constant to metal ions, such as ethylenediaminetetraacetic acid and nitrilotriacetic acid.

024]

Effect of the Invention] By this invention, conventionally, analysis of analysis of the anions and metal ions for which two or more analysis apparatus and conditions were required is simultaneously attained on one set of an analysis apparatus, and one analysis condition, and simultaneous analysis of anions and metal ions is attained for a short time (an example 7 minutes).

[translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the approach and equipment which analyze ion using capillary electrophoresis, and relates to the ion analytical method and equipment by capillary electrophoresis which can measure ions, such as an organic acid, a fatty acid, aromatic carboxylic acid, and an inorganic anion, and metal ions, such as nickel, cobalt, copper, and zinc, to coincidence especially.

[translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

PRIOR ART

Description of the Prior Art] Conventionally, anion nature matter, such as an organic acid and an inorganic anion, was measured using separation analysis equipments, such as ion chromatography and capillary electrophoresis, and, on the other hand, the cation nature matter containing metal ions, such as nickel, cobalt, and copper, was measured using separation analysis equipments, such as elemental-analysis equipments, such as atomic-absorption-analysis equipment, inductively-coupled-plasma-atomic-emission-spectrometry equipment (ICP/AES), and inductively-coupled-plasma-source-mass-spectrometry equipment (ICP/MS), or ion chromatography, and capillary electrophoresis.

[translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] By this invention, conventionally, analysis of analysis of the anions and metal ions for which 10 or more analysis apparatus and conditions were required is attained on one set of an analysis apparatus, and one analysis condition at coincidence, and coincidence analysis of anions and metal ions is attained for a short time (an example 7 minutes).

[translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

TECHNICAL PROBLEM

Problem(s) to be Solved by the Invention] However, since the anions and metal ions from which ionicity differs were not able to be measured to coincidence, a measuring device and conditions were required for at least two, and the number of equipment needed to increase, or it needed to measure by having changed the Measuring condition, and had troubles, like measurement takes time amount.

004] This invention was made so that it may cancel said conventional trouble, and it makes it a technical problem to enable it to analyze anions and metal ions to coincidence using capillary electrophoresis.

Translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] This invention solves said technical problem by facing analyzing ion using capillary electrophoresis, using for the migration buffer solution the anion nature matter which has a high complex stability constant to metal ions, and making the complex of metal ions and anion nature form.

[0006] Moreover, let said anion nature matter be 2, 6-pyridinecarboxylic acid, ethylenediaminetetraacetic acid, or nitrilotriacetic acid.

[0007] Moreover, similarly in the equipment which analyzes ion using capillary electrophoresis, said technical problem is solved by having the migration buffer solution with which the anion nature matter which has a high complex stability constant to metal ions was used, the capillary which separates the ion poured into this migration buffer solution, and the detector which analyzes the separated anions and metal ions to coincidence by this capillary appearance side.

[0008] Moreover, it can be made to perform highly precise measurement with a single detector by using said detector as the diode array detector in which measurement by both indirect extinction method and direct detection method is possible.

[0009] 2, 6-pyridinecarboxylic acid (PDC), ethylenediaminetetraacetic acid, It is a high complex stability constant (it is used best as what shows the stability in the solution of a complex) to metal ions, such as nitrilotriacetic acid. it expresses with the inverse number of the dissociation constant of a complex -- having -- it has, and by using the high anion nature matter of metal ions and complexing ability for the migration buffer solution (buffer), the nickel in a sample, cobalt, a copper ion, etc. form PDC and a complex, and as shown in drawing 1, they show anion nature. Therefore, it becomes possible to measure to an organic acid and coincidence, such as inorganic anions, such as chloride ion and sulfate ion, and malic acid, a citric acid, an acetic acid.

[0010] The complex stability constant to each metal of PDC which can be used for a buffer is shown in drawing 2.

[0011] For example, PDC metal complexes, such as PDC and nickel, have ultraviolet (UV) absorption, and in the wavelength of 275nm, and 225nm, since UV absorption is larger than PDC of a buffer, as shown in drawing 3 (A), a peak appears above the base line. On the other hand, in anions, since UV absorption is smaller than PDC, a peak appears below the base line. However, by choosing measurement wavelength, the upper and lower sides can be reversed, and as shown in drawing 3 (B), anions can also be expressed to the bottom.

[0012] Drawing 3 (A) is the case where drawing 3 (B) is based on the indirect extinction method of the measurement wavelength of 350.20nm, and 275.10nm of reference wave length, when based on the measurement wavelength of 275.10nm, and the direct detection method of reference wave length OFF.

[0013]

[Embodiment of the Invention] With reference to a drawing, the operation gestalt of this invention is explained to a detail below.

[0014] The whole ion analysis apparatus configuration by the capillary electrophoresis built over this invention at drawing 4 is shown.

[0015] This operation gestalt with the capillary 10 for separating a sample, and the sample 6 in a specimen container 8. The buffers 12 (cathode side) and 13 (anode plate side) for being introduced into this capillary 10 and separating a sample. To the platinum electrodes 16 (cathode side) and 17 (anode plate side) of said capillary 10 both ends, for example, the high voltage power supply 14 which impresses the high voltage of 5-30kV. It is constituted including the cell 1 for detection which removed the outer wall (for example, polyimide) of said capillary 10, and was formed, and UV diode array detector 20 in which measurement by both indirect extinction method and direct detection method is possible.

016] The sample 6 inserted in said specimen container 8 is poured into the buffer 12 by the side of cathode by sealing y covering with a lid 9 to this specimen container 8, and pressurizing the inside of a specimen container, as shown in rawing 5 . Since the complexing reaction of PDC in a buffer is quick, if a sample 6 is poured in into a capillary 10 and ixed with PDC, a complex will be formed immediately.

017] The light source 22 which consists of deuterium lamps as said UV diode array detector 20 is shown in a detail at rawing 6 , The lens 24 for making into a parallel ray light generated from this light source 22, the shutter 26 for turning a measuring beam line on and off, and the cel 11 for detection of said capillary 10 by the way The optical slit 28 for an lignment interface for ready-*(ing) a measuring beam line, It is constituted using the diode array 32 whose measurement wavelength is 190-600nm in order to detect the light diffracted by the diffraction grating 30 and this iffraction grating 30 for diffracting the measuring beam line which passed this optical slit 28 according to wavelength or every wavelength.

[translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] This invention solves said technical problem by facing analyzing ion using capillary electrophoresis, using for the migration buffer solution the anion nature matter which has a high complex stability constant to metal ions, and making the complex of metal ions and anion nature form.

[0006] Moreover, let said anion nature matter be 2, 6-pyridinecarboxylic acid, ethylenediaminetetraacetic acid, or nitrilotriacetic acid.

[0007] Moreover, similarly in the equipment which analyzes ion using capillary electrophoresis, said technical problem is solved by having the migration buffer solution with which the anion nature matter which has a high complex stability constant to metal ions was used, the capillary which separates the ion poured into this migration buffer solution, and the detector which analyzes the separated anions and metal ions to coincidence by this capillary appearance side.

[0008] Moreover, it can be made to perform highly precise measurement with a single detector by using said detector as a diode array detector in which measurement by both indirect extinction method and direct detection method is possible.

[0009] 2, 6-pyridinecarboxylic acid (PDC), ethylenediaminetetraacetic acid, It is a high complex stability constant (it is expressed best as what shows the stability in the solution of a complex) to metal ions, such as nitrilotriacetic acid. It expresses with the inverse number of the dissociation constant of a complex -- having -- it has, and by using the high anion nature matter of metal ions and complexing ability for the migration buffer solution (buffer), the nickel in a sample, cobalt, a copper ion, etc. form PDC and a complex, and as shown in drawing 1, they show anion nature. Therefore, it becomes possible to measure to an organic acid and coincidence, such as inorganic anions, such as chloride ion and sulfate ion, and malic acid, a citric acid, an acetic acid.

[0010] The complex stability constant to each metal of PDC which can be used for a buffer is shown in drawing 2.

[0011] For example, PDC metal complexes, such as PDC and nickel, have ultraviolet (UV) absorption, and in the wavelength of 275nm, and 225nm, since UV absorption is larger than PDC of a buffer, as shown in drawing 3 (A), a peak appears above the base line. On the other hand, in anions, since UV absorption is smaller than PDC, a peak appears below the base line. However, by choosing measurement wavelength, the upper and lower sides can be reversed, and as shown in drawing 3 (B), anions can also be expressed to the bottom.

[0012] Drawing 3 (A) is the case where drawing 3 (B) is based on the indirect extinction method of the measurement wavelength of 350.20nm, and 275.10nm of reference wave length, when based on the measurement wavelength of 75.10nm, and the direct detection method of reference wave length OFF.

[0013]

[Embodiment of the Invention] With reference to a drawing, the operation gestalt of this invention is explained to a detail below.

[0014] The whole ion analysis apparatus configuration by the capillary electrophoresis built over this invention at drawing 4 is shown.

[0015] This operation gestalt with the capillary 10 for separating a sample, and the sample 6 in a specimen container 8. The buffers 12 (cathode side) and 13 (anode plate side) for being introduced into this capillary 10 and separating a sample. To the platinum electrodes 16 (cathode side) and 17 (anode plate side) of said capillary 10 both ends, for example, the high voltage power supply 14 which impresses the high voltage of 5-30kV. It is constituted including the cell 1 for detection which removed the outer wall (for example, polyimide) of said capillary 10, and was formed, and UV diode array detector 20 in which measurement by both indirect extinction method and direct detection method is possible.

016] The sample 6 inserted in said specimen container 8 is poured into the buffer 12 by the side of cathode by sealing y covering with a lid 9 to this specimen container 8, and pressurizing the inside of a specimen container, as shown in rawing 5 . Since the complexing reaction of PDC in a buffer is quick, if a sample 6 is poured in into a capillary 10 and mixed with PDC, a complex will be formed immediately.

017] The light source 22 which consists of deuterium lamps as said UV diode array detector 20 is shown in a detail at rawing 6 , The lens 24 for making into a parallel ray light generated from this light source 22, the shutter 26 for turning a measuring beam line on and off, and the cel 11 for detection of said capillary 10 by the way The optical slit 28 for an alignment interface for ready-*(ing) a measuring beam line, It is constituted using the diode array 32 whose measurement wavelength is 190-600nm in order to detect the light diffracted by the diffraction grating 30 and this diffraction grating 30 for diffracting the measuring beam line which passed this optical slit 28 according to wavelength or every wavelength.

[translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

EXAMPLE

Example] As buffers 12 and 13, 20mMPDC and the 0.5mM cetyl trimethylammonium star's picture pH 5.77 were used, using the fuze DOSHIRIKA capillary of the bore of 50 micrometers, the outer diameter of 350 micrometers, the overall length of 80.5cm, and 72cm of effective length to the cell 11 for detection as said capillary 10. Applied voltage measured the temperature of 25kV and a capillary 10 at 20 degrees C. The sample was poured in for 8 seconds by 50mbar using the inflatable flexible bag technique as shown in drawing 5. The indirect extinction method of the measurement wavelength of 350.20nm and 275.10nm of reference wave length was used for detection of the matter which has almost no UV absorption like sulfate ion or organic acids in detection of the matter which has UV absorption like nickel ion in detection using UV diode array detector 20 using the measurement wavelength of 275.10nm, and the direct detection method of reference wave long OFF. Drawing 3 shows the example of measurement of the organic-acid standard solution in this example.

0019] Moreover, the example of coincidence analysis of the anions in the non-electrolyzed nickel-plating liquid diluted 100 times and nickel ion is shown in drawing 7.

0020] The approach of this operation gestalt and the comparison result of the quantum value of the nickel in the non-electrolyzed nickel-plating liquid measured by conventional ICP/MS are shown in drawing 8. Both analysis result is well in agreement so that clearly from drawing.

0021] Moreover, the example of coincidence analysis of the anions in the non-electrolytic copper plating liquid of 500 time dilution and a copper ion is shown in drawing 9.

0022] In this operation gestalt, since UV diode array detector is used as a detector, measurement by both indirect extinction method and direct detection method is possible at one detector, and a configuration is simple.

0023] In addition, the class of detector is not limited to this. Measurement wavelength is also limited to neither an operation gestalt nor an example. The class of capillary is not limited to a fuze DOSHIRIKA capillary, either. It is possible to use other anion nature matter in which a buffer is not limited to PDC, either but has a high complex stability constant to metal ions, such as ethylenediaminetetraacetic acid and nitrilotriacetic acid.

Translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

Drawing 1] The diagram showing an example of the complex formed by the buffer for explaining the principle of this invention

Drawing 2] The graph showing the complex stability constant to each metal of PDC which is an example of a buffer

Drawing 3] The diagram showing the example of measurement of the organic-acid standard solution for explaining the principle of this invention

Drawing 4] The sectional view showing the whole ion analysis apparatus configuration by the capillary electrophoresis of the operation gestalt concerning this invention

Drawing 5] The sectional view showing the sample impregnation approach to the capillary in said operation gestalt

Drawing 6] The perspective view showing the configuration of UV diode array detector used with said operation gestalt

Drawing 7] The diagram showing the example of analysis of the non-electrolyzed nickel-plating liquid by this invention

Drawing 8] The graph comparing and showing the quantum value of the nickel in the non-electrolyzed nickel-plating liquid measured by this invention method and ICP-MS to show the usefulness of this invention

Drawing 9] The diagram showing the example of measurement in the non-electrolytic copper plating liquid by this invention

[Description of Notations]

-- Sample

-- Specimen container

0 -- Capillary

2 13 -- Buffer

4 -- High voltage power supply

6 17 -- Platinum electrode

0 -- UV diode array detector

2 -- Light source

0 -- Diffraction grating

2 -- Diode array

[Translation done.]

NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

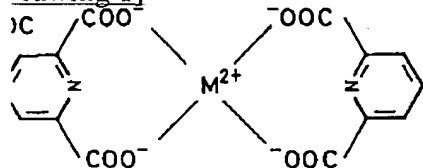
This document has been translated by computer. So the translation may not reflect the original precisely.

**** shows the word which can not be translated.

In the drawings, any words are not translated.

RAWINGS

Drawing 1]

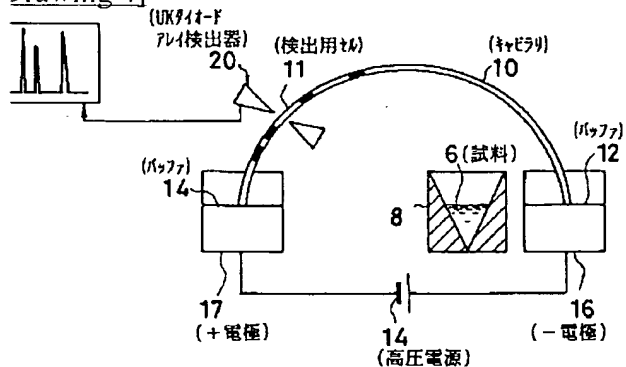


Drawing 2]

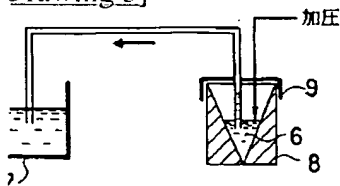
錯安定度定数 $\log K_1$

Ca	4.6
Co (I)	7.0
Cu (II)	9.14
Fe (II)	5.71
Fe (III)	10.91
Mg	2.9
Ni	6.95
Pb	8.70
Zn	6.35

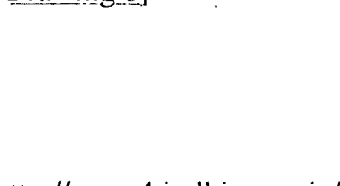
Drawing 4]

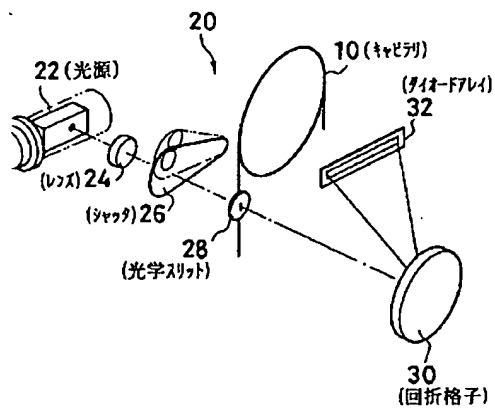


Drawing 5]

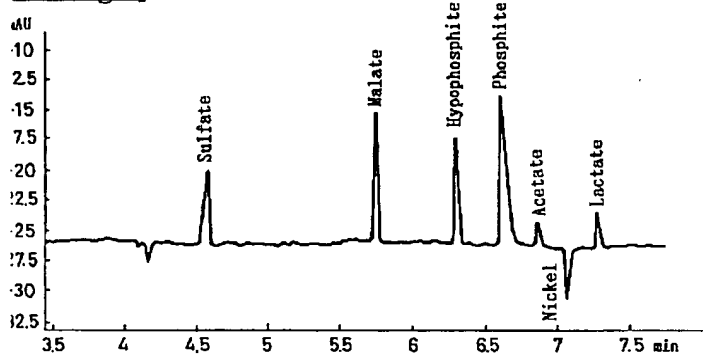


Drawing 6]





Drawing 7]

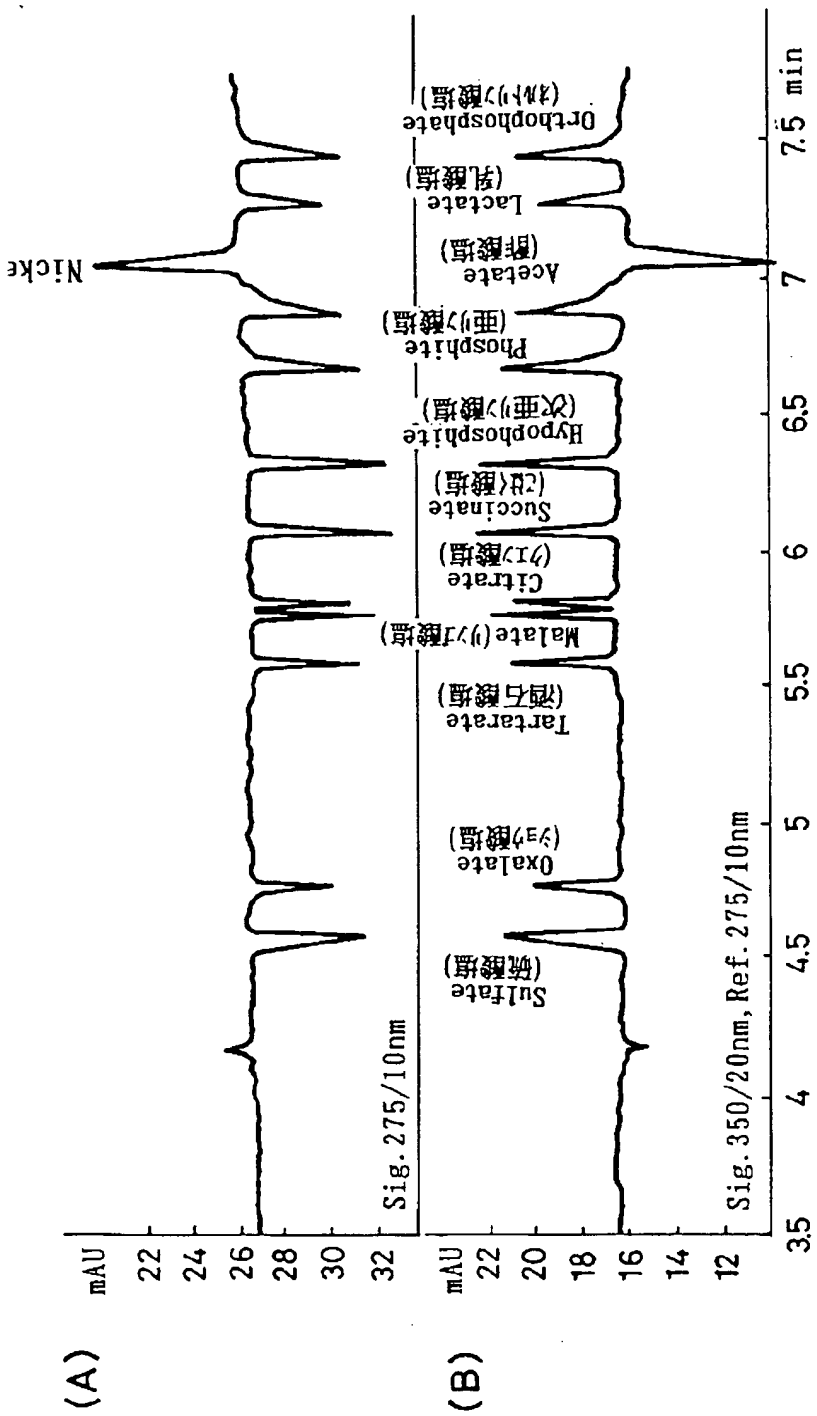


Drawing 8]

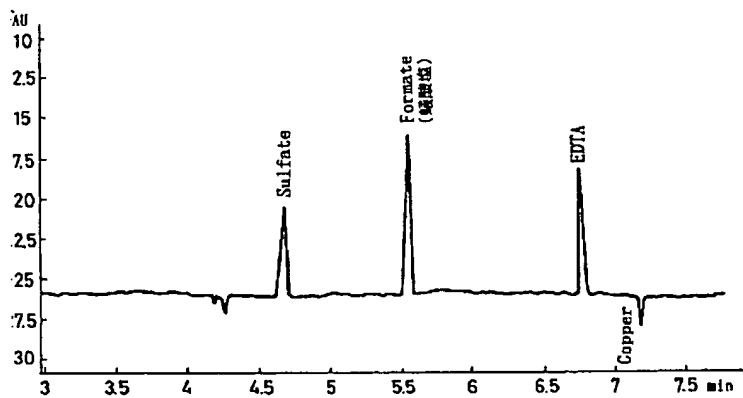
(単位 g/l)

	本発明法	ICP/MS (従来法)
試料 A	6.6	6.3
試料 B	5.0	5.0
試料 C	6.5	6.5
試料 D	6.3	6.3

Drawing 3]



Drawing 9]



[translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平11-118761

(43) 公開日 平成11年(1999) 4月30日

(51) Int. Cl.⁶

G 0 1 N 27/447

識別記号

P I

G 0 1 N 27/26

3 3 1 E

3 0 1 B

3 3 1 K

審査請求 未請求 請求項の数 4 O L (全 6 頁)

(21) 出願番号

特願平9-281526

(22) 出願日

平成9年(1997)10月15日

(71) 出願人 392016317

横河アナリティカルシステムズ株式会社
東京都武蔵野市中町1丁目15番5号 三鷹
高木ビル

(72) 発明者 曾我 朋義

東京都武蔵野市中町一丁目15番5号 三鷹
高木ビル 横河アナリティカルシステムズ
株式会社内

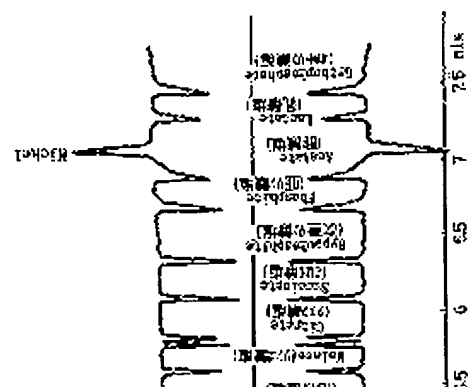
(74) 代理人 弁理士 高矢 諭 (外2名)

(54) 【発明の名称】 キャピラリ電気泳動によるイオン類分析方法及び装置

(57) 【要約】

【課題】 有機酸と無機陰イオン等の陰イオン類と、ニッケル、コバルト、銅等の金属イオン類を同時に分析可能とする。

【解決手段】 金属イオン類に対して高い錯安定度数を持つ陰イオン性物質をバッファ12、13に用いて、金属イオン類と陰イオン性の錯体を形成させる。



【特許請求の範囲】

【請求項1】キャピラリ電気泳動を用いてイオン類を分析するに際して、

金属イオン類に対して高い錯安定度定数を持つ陰イオン性物質を泳動緩衝液に用いて、金属イオン類と陰イオン性の錯体を形成させることにより、

陰イオン類と金属イオン類を同時に分析することを特徴とするキャピラリ電気泳動によるイオン類分析方法。

【請求項2】請求項1において、前記陰イオン性物質が、2、6-ピリジンカルボン酸、エチレンジアミン四酢酸、又は、ニトリロ三酢酸であることを特徴とするキャピラリ電気泳動によるイオン類分析方法。

【請求項3】キャピラリ電気泳動を用いてイオン類を分析する装置において、

金属イオン類に対して高い錯安定度定数を持つ陰イオン性物質が用いられた泳動緩衝液と、

該泳動緩衝液に注入されたイオン類を分離するキャピラリと、

該キャピラリ出側で、分離された陰イオン類と金属イオン類を同時に分析する検出器と、

を備えたことを特徴とするキャピラリ電気泳動によるイオン類分析装置。

【請求項4】請求項3において、前記検出器が、間接吸光度法及び直接検出法の両者による測定が可能なダイオードアレイ検出器であることを特徴とするキャピラリ電気泳動によるイオン類分析装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、キャピラリ電気泳動を用いてイオン類を分析する方法及び装置に係り、特に、有機酸、脂肪酸、芳香族カルボン酸、無機陰イオン等の陰イオン類と、ニッケル、コバルト、銅、亜鉛等の金属イオン類を同時に測定することが可能な、キャピラリ電気泳動によるイオン類分析方法及び装置に関する。

【0002】

【従来の技術】従来、有機酸、無機陰イオン等の陰イオン性物質は、イオンクロマトグラフィやキャピラリ電気泳動等の分離分析装置を用いて測定され、一方、ニッケル、コバルト、銅等の金属イオン類を含む陽イオン性物質は、原子吸光分析装置、誘導結合プラズマ原子発光分

【0004】本発明は、前記従来の問題点を解消するべくなされたもので、キャピラリ電気泳動を用いて、陰イオン類と金属イオン類を同時に分析できるようにすることを課題とする。

【0005】

【課題を解決するための手段】本発明は、キャピラリ電気泳動を用いてイオン類を分析するに際して、金属イオン類に対して高い錯安定度定数を持つ陰イオン性物質を泳動緩衝液に用いて、金属イオン類と陰イオン性の錯体を形成させることにより、前記課題を解決したものである。

【0006】又、前記陰イオン性物質を、2、6-ピリジンカルボン酸、エチレンジアミン四酢酸、又は、ニトリロ三酢酸としたものである。

【0007】又、キャピラリ電気泳動を用いてイオン類を分析する装置において、金属イオン類に対して高い錯安定度定数を持つ陰イオン性物質が用いられた泳動緩衝液と、該泳動緩衝液に注入されたイオン類を分離するキャピラリと、該キャピラリ出側で、分離された陰イオン類と金属イオン類を同時に分析する検出器とを備えることにより、同じく前記課題を解決したものである。

【0008】又、前記検出器を、間接吸光度法及び直接検出法の両者による測定が可能なダイオードアレイ検出器とすることにより、単一の検出器で高精度の測定ができるようにしたものである。

【0009】2、6-ピリジンカルボン酸（PDC）、エチレンジアミン四酢酸、ニトリロ三酢酸等の、金属イオン類に対して高い錯安定度定数（錯体の溶液中における安定度を示すものとして最もよく用いられ、錯体の解離定数の逆数で表わされる）を持ち、金属イオン類と錯体形成能の高い陰イオン性物質を泳動緩衝液（バッファ）に用いることで、試料中のニッケル、コバルト、銅イオン等は、例えばPDCと錯体を形成し、図1に示す如く陰イオン性を示す。従って、塩化物イオンや硫酸イオン等の無機陰イオン類や、リンゴ酸、クエン酸、酢酸等の有機酸と同時に測定することが可能となる。

【0010】バッファに用いることが可能なPDCの各金属に対する錯安定度定数を図2に示す。

【0011】例えばPDCとニッケル等のPDC金属錯体は、紫外（UV）吸収を持ち、波長275nm及び2

nmの間接吸光度法による場合である。

【0013】

【発明の実施の形態】以下図面を参照して、本発明の実施形態を詳細に説明する。

【0014】図4に、本発明にかかるキャピラリ電気泳動によるイオン類分析装置の全体構成を示す。

【0015】本実施形態は、試料の分離を行うためのキャピラリ10と、試料容器8中の試料6と共に、該キャピラリ10の中へ導入され、試料を分離するためのバッファ12（陰極側）、13（陽極側）と、前記キャピラリ10両端の、例えば白金電極16（陰極側）、17（陽極側）に例えば5〜30kVの高電圧を印加する高圧電源14と、前記キャピラリ10の外壁（例えばポリイミド）を剥がして形成された検出用セル11と、間接吸光度法及び直接検出法の両者による測定が可能なりUVダイオードアレイ検出器20とを含んで構成されている。

【0016】前記試料容器8に装入された試料6は、図5に示す如く、該試料容器8に蓋9をして密閉し、試料容器内を加圧することによって、陰極側のバッファ12に注入される。バッファ中のPDCの錯体形成反応は速いため、試料6がキャピラリ10内に注入され、PDCと混合すると、即座に錯体が形成される。

【0017】前記UVダイオードアレイ検出器20は、図6に詳細に示す如く、例えば重水素ランプで構成される光源22と、該光源22から発生された光を平行光線とするためのレンズ24と、測定光線をオン・オフするためのシャッタ26と、前記キャピラリ10の検出用セル11のところで、測定光線を整向するためのアライメントインターフェース用光学スリット28と、該光学スリット28を通過した測定光線を波長に応じて回折するための回折格子30と、該回折格子30によって回折された光を波長毎に検出するための、例えば測定波長が190〜600nmのダイオードアレイ32とを用いて構成されている。

【0018】

【実施例】前記キャピラリ10として、内径50μm、外径350μm、全長80.5cm、検出用セル11までの有効長72cmのフューズドシリカキャピラリを用い、バッファ12、13としては、20mMPDC、

用いた。図3は、本実施例における有機酸標準液の測定例を示したものである。

【0019】又、500倍に希釈した無電解ニッケルめっき液中の陰イオン類とニッケルイオンの同時分析例を図7に示す。

【0020】本実施形態の方法と、従来のICP/MSで測定した無電解ニッケルめっき液中のニッケルの定置値の比較結果を図8に示す。図から明らかな如く、両者の分析結果は、よく一致している。

【0021】又、500倍希釈の無電解銅めっき液中の陰イオン類と銅イオンの同時分析例を図9に示す。

【0022】本実施形態においては、検出器としてUVダイオードアレイ検出器を用いているので、間接吸光度法及び直接検出法の両者による測定が1台の検出器で可能であり、構成が簡略である。

【0023】なお、検出器の種類はこれに限定されない。測定波長も、実施形態や実施例に限定されない。キャピラリの種類も、フューズドシリカキャピラリに限定されない。バッファもPDCに限定されず、エチレンジアミン四酢酸、ニトリロ三酢酸等の、金属イオン類に対して高い錯安定度定数を持つ他の陰イオン性物質を用いることが可能である。

【0024】

【発明の効果】本発明により、従来は、2つ以上の分析装置、条件が必要であった陰イオン類と金属イオン類の分析が、1台の分析装置、1つの分析条件で同時に分析可能となり、短時間（実施例では7分）で陰イオン類と金属イオン類の同時分析が可能になる。

【図面の簡単な説明】

【図1】本発明の原理を説明するための、バッファによって形成される錯体の一例を示す線図

【図2】バッファの一例であるPDCの各金属に対する錯安定度定数を示す図表

【図3】本発明の原理を説明するための、有機酸標準液の測定例を示す線図

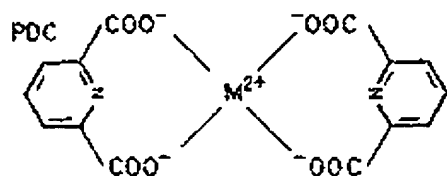
【図4】本発明に係る実施形態のキャピラリ電気泳動によるイオン類分析装置の全体構成を示す断面図

【図5】前記実施形態におけるキャピラリへの試料注入方法を示す断面図

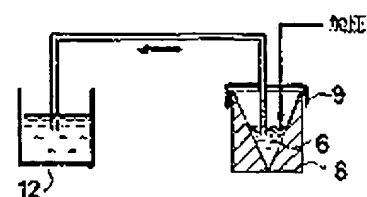
【図6】前記実施形態で用いられているUVダイオード

* 20…UVダイオードアレイ検出器
22…光源
30…回折格子
32…ダイオードアレイ

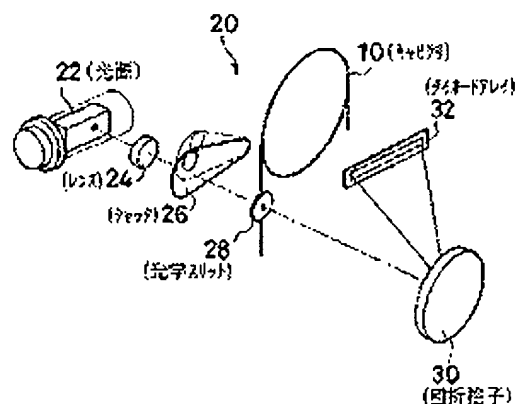
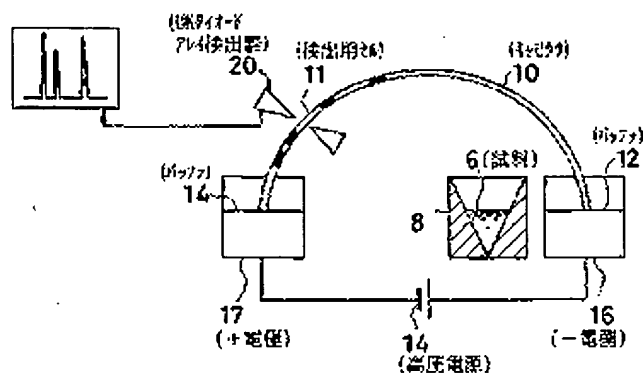
【图5】



	測定定数 log K _f
Ca	4.6
Co (I)	7.0
Cu (II)	9.14
Fe (II)	5.71
Fe (III)	10.91
Mg	2.9
Ni	6.95
Pb	8.70
Zn	6.35



【図6】

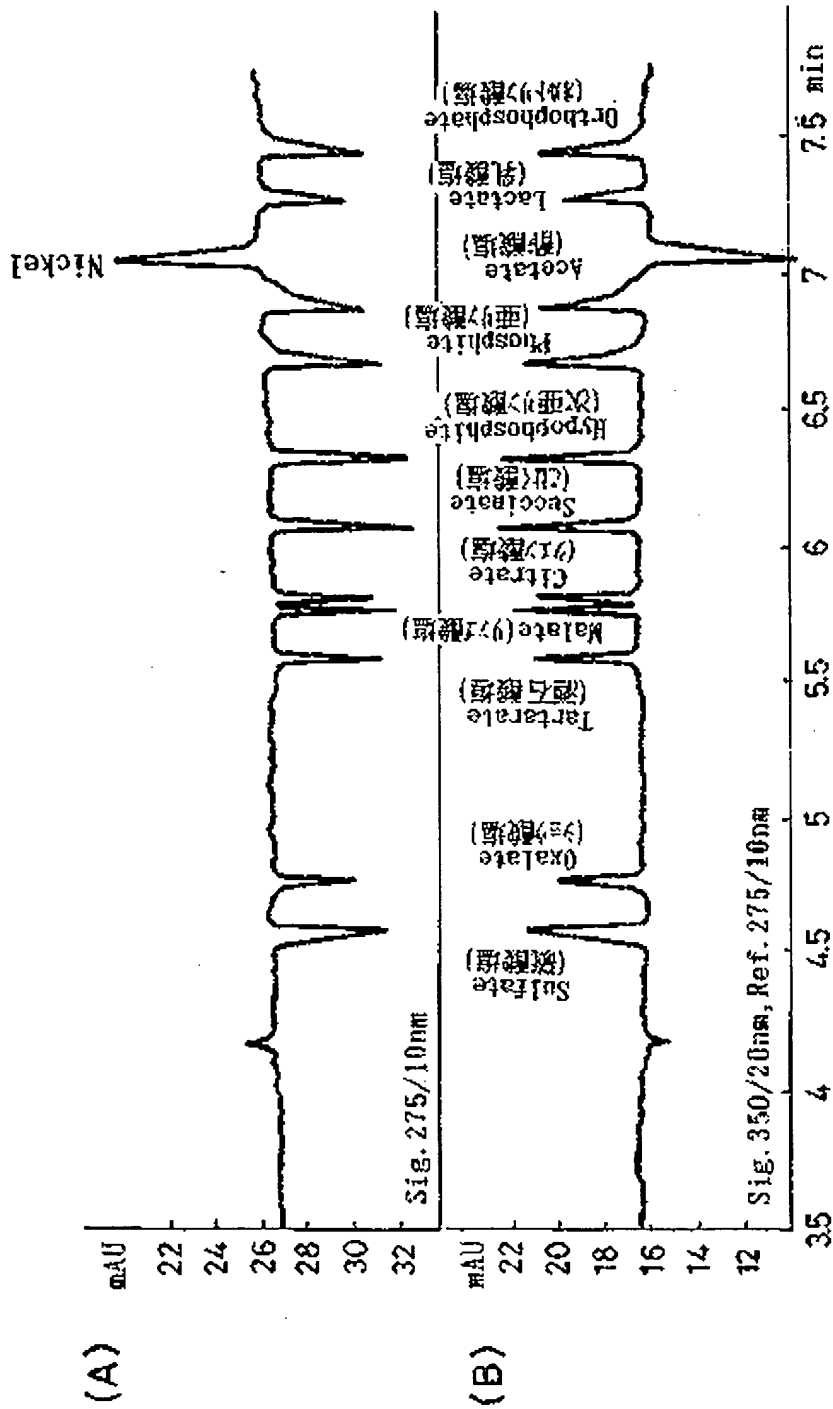


【例8】



(单位 g/l)	
本实验室	ICP/MS (参考法)
0.000	0.000
0.001	0.001
0.002	0.002
0.003	0.003
0.004	0.004
0.005	0.005
0.006	0.006
0.007	0.007
0.008	0.008
0.009	0.009
0.010	0.010
0.011	0.011
0.012	0.012
0.013	0.013
0.014	0.014
0.015	0.015
0.016	0.016
0.017	0.017
0.018	0.018
0.019	0.019
0.020	0.020
0.021	0.021
0.022	0.022
0.023	0.023
0.024	0.024
0.025	0.025
0.026	0.026
0.027	0.027
0.028	0.028
0.029	0.029
0.030	0.030
0.031	0.031
0.032	0.032
0.033	0.033
0.034	0.034
0.035	0.035
0.036	0.036
0.037	0.037
0.038	0.038
0.039	0.039
0.040	0.040
0.041	0.041
0.042	0.042
0.043	0.043
0.044	0.044
0.045	0.045
0.046	0.046
0.047	0.047
0.048	0.048
0.049	0.049
0.050	0.050
0.051	0.051
0.052	0.052
0.053	0.053
0.054	0.054
0.055	0.055
0.056	0.056
0.057	0.057
0.058	0.058
0.059	0.059
0.060	0.060
0.061	0.061
0.062	0.062
0.063	0.063
0.064	0.064
0.065	0.065
0.066	0.066
0.067	0.067
0.068	0.068
0.069	0.069
0.070	0.070
0.071	0.071
0.072	0.072
0.073	0.073
0.074	0.074
0.075	0.075
0.076	0.076
0.077	0.077
0.078	0.078
0.079	0.079
0.080	0.080
0.081	0.081
0.082	0.082
0.083	0.083
0.084	0.084
0.085	0.085
0.086	0.086
0.087	0.087
0.088	0.088
0.089	0.089
0.090	0.090
0.091	0.091
0.092	0.092
0.093	0.093
0.094	0.094
0.095	0.095
0.096	0.096
0.097	0.097
0.098	0.098
0.099	0.099
0.100	0.100
0.101	0.101
0.102	0.102
0.103	0.103
0.104	0.104
0.105	0.105
0.106	0.106
0.107	0.107
0.108	0.108
0.109	0.109
0.110	0.110
0.111	0.111
0.112	0.112
0.113	0.113
0.114	0.114
0.115	0.115
0.116	0.116
0.117	0.117
0.118	0.118
0.119	0.119
0.120	0.120
0.121	0.121
0.122	0.122
0.123	0.123
0.124	0.124
0.125	0.125
0.126	0.126
0.127	0.127
0.128	0.128
0.129	0.129
0.130	0.130
0.131	0.131
0.132	0.132
0.133	0.133
0.134	0.134
0.135	0.135
0.136	0.136
0.137	0.137
0.138	0.138

【図3】



(6)

特開平11-118761

【図9】

